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## Emissions from Diesel Vehicles with and without Lean NO<sub>x</sub> and Oxidation Catalysts and Particulate Traps

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# Emissions from Diesel Vehicles with and without Lean NO<sub>x</sub> and Oxidation Catalysts and Particulate Traps

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## ABSTRACT

The regulated and non-regulated emissions of a current diesel passenger car and two light-duty diesel trucks with catalysts and particulate traps were measured to better understand the effects of aftertreatment devices on the environment. The passenger car, a 1.8 L IDI TC Sierra, was tested both with and without three different diesel oxidation catalysts (DOC) and with two fuel sulfur levels, 0 and 0.05 wt%. One light-duty truck, a 2.5 L DI NA Transit, was tested on one fuel, 0.05 wt% sulfur, with and without three different particulate trap/regeneration systems and with and without a urea lean NO<sub>x</sub> catalyst (LNC) system. A second similar Transit was tested on the 0.05 wt% sulfur fuel with an electrically regenerated trap system. The results are compared to each other, regulated emission standards, and to emissions from gasoline vehicles.

## INTRODUCTION

This work is a continuation of earlier work (1)\* that compared the emissions of 1993 light-duty diesel vehicles to that from similar model gasoline vehicles. The earlier work used a full complement of analytical methods to characterize the emissions, including HC, CO, NO<sub>x</sub>, particulate matter (PM), CO<sub>2</sub>, C<sub>1</sub> to C<sub>12</sub> species (here called light hydrocarbon or LHC), aldehydes, particulate composition and particulate size distribution. The particulate composition measurements included elemental

carbon (EC or soot), soluble organic fraction (SOF), oil, fuel and sulfate fractions, and polycyclic aromatic hydrocarbons (PAH). The emissions were measured on both the European (MVEG or ECE-15 plus EUDC) and the U.S. Federal test procedures (FTP75).

The diesel vehicles tested in that work had lower HC, CO, CO<sub>2</sub>, CH<sub>4</sub>, NMOG, benzene and 1,3 butadiene emissions than the gasoline vehicles, but had higher NO<sub>x</sub>, PM and aldehyde emissions. This work uses the same analytical methods to examine emissions from vehicles with aftertreatment technologies that appear capable of reducing the diesel NO<sub>x</sub>, PM and aldehyde emissions to the level of gasoline vehicles. Specifically, emission improvements due to prototype particulate traps, DOC and LNC are measured. There are earlier reports of diesel emissions with traps (2,3) and DOC (4,5,6) but these have more limited non-regulated emissions measurements than this work. The LNC system measured here uses urea as the reductant (7,8). The durabilities of these traps and catalyst systems have not been proven.

The main objective of this work is to help determine the potential for diesel vehicles to have equal, or lower, impact on the environment than gasoline vehicles.

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\* Numbers in parentheses designate references at the end of the paper.

## METHODS

**VEHICLES** - The passenger car used here was a 1992 production Sierra with a 1.8 L IDI TC diesel engine. This vehicle which is a typical European passenger car was used to test the DOC. Its odometer read about 25,000 km, and it was tested at 1360 kg inertia weight. The catalysts were located about 100 cm downstream of the turbocharger outlet. The vehicle was described more completely elsewhere (9). Two Transits were used to test both the urea LNC and the traps because some of these systems required more space than the Sierra provided. The Transits are typical European light-duty trucks. Both had 2.5 L NA DI diesel engines with maximum power of 52 kw (70 HP) and were tested at 1820 kg inertia weight. A 1993 production Transit was used for the traps with fuel additive regeneration and the urea LNC. It was equipped with a 66 in<sup>3</sup> (1.08 L) Degussa DOC with 40 g/ft<sup>3</sup> of platinum located in the production underbody position, Table 1. This vehicle had about 2,000 km on the odometer. A 1992 production Transit was used for the electrically regenerated particulate trap testing. It had over 10,000 km on the odometer and did not have a catalyst. It is described more completely elsewhere (1).

Three DOC were tested on the Sierra, Table I. Two DOC, one from Degussa and the other from Johnson Matthey, used 40 and 50 g/ft<sup>3</sup> of platinum, respectively, as the active metal. Both platinum catalysts used 300 cells/in<sup>2</sup> substrates. The third DOC from AC Rochester used 50 g/ft<sup>3</sup> palladium and a 400 cells/in<sup>2</sup> substrate. All of the DOC had the same volume, 46 in<sup>3</sup> (0.75 L). Tests without

a catalyst were conducted using an empty exhaust pipe in place of the catalyst.

One urea LNC was tested on the 1993 Transit (8); it was made by Siemens in a 200 cell/in<sup>2</sup> ceramic honeycomb structure made of a uniform mixture of V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and WO<sub>3</sub>. Its volume was 451 in<sup>3</sup> (7.4 L) and its geometric surface area was 11.8 m<sup>2</sup>. The urea, which was needed to reduce the NO<sub>x</sub>, was added to the exhaust system before the LNC with an air-assisted injector.

Several Corning traps were tested on the 1993 Transit which used fuel additives to promote regeneration (10). These traps were 100 cells/in<sup>2</sup>, 17 mil wall, EX 47, cordierite traps, 7.5 in OD by 8 in long. Their volume was 353 in<sup>3</sup> (5.8 L), and their geometric surface area was 3.8 m<sup>2</sup>. In addition, a SHW trap was tested on this Transit. This trap was a sintered metal trap with 46 plates, each about 3.5 in wide by 10.6 in long. Its volume was 172 in<sup>3</sup> (2.8 L) and its geometric surface area was 0.9 m<sup>2</sup>. These traps were located as close to the engine as possible, approximately 15 cm from the exhaust manifold flange. This configuration which may not be possible in production was used to represent the best possible performance.

The fuel additive concentrations were 67 ppm Fe by weight as ferrocene or 50 ppm K by weight as alkyl salicylate. The fuel and additives were blended in an external tank and the blend used to fill the vehicle tank.

Table I. Catalyst Descriptions

Source	Test Vehicle	Active Material	Noble Metal Loading (g/ft <sup>3</sup> )	Catalyst Volume (L)	Substrate (cells/in <sup>2</sup> )
Degussa	Sierra	Pt	40	0.75	300
	1993 Transit	Pt	40	1.08	300
AC Rochester (AC)	Sierra	Pd	50	0.75	400
Johnson Matthey (JMI)	Sierra	Pt	50	0.75	300
Siemens	1993 Transit	V <sub>2</sub> O <sub>5</sub> , TiO <sub>2</sub> , WO <sub>3</sub>	0	7.4	200

The Transit was driven with each fuel additive 3200 km to stabilize engine and exhaust system deposits before emissions testing.

The electrically regenerated trap was tested on the 1992 Transit. The trap was separated into 66 segments, each segment included 60 open and 44 closed channels which extend from the trap inlet to exit (11). Each segment had a 600 watt electrical heater mounted in its inlet. Regeneration of one segment began at the inlet when its heater is turned on for 40 seconds and then continued in a self-sustaining manner toward the exit after the heater was turned off. Regeneration of the segments occurred uniformly in time to maintain a constant back pressure. Exhaust gas continued to flow through the trap during regeneration. Three Corning EX 47 traps 7.5 in OD by 4 in long with 22 segments each were mounted in parallel. The overall trap volume is 530 in<sup>3</sup> (8.7 L) and its area is 5.7 m<sup>2</sup>.

**METHODS AND TEST EQUIPMENT** - The analytical methods, which were used here, have been described in an earlier paper (12). The chassis dynamometer and dilution tube were also described elsewhere (1).

Two basic fuels were used; one was a typical European diesel fuel with 0.05 wt% sulfur and the other was a Swedish Class 1 fuel with 0.00 wt% sulfur (13). All testing on the Sierra used the Swedish Class 1 fuel as the base, but in some tests the fuel was doped with sulfur compounds to the 0.05 wt% level. All testing on the Transits used the typical European fuel with 0.05 wt% sulfur.

## RESULTS AND DISCUSSION

### CATALYSTS

**REGULATED EMISSIONS** - On the Sierra, the DOC substantially reduced the HC and CO emissions and slightly reduced the PM emissions as expected, Table II. For example, the HC emissions were reduced from about 0.1 g/km (0.15 g/mi) on the European procedure without a catalyst to about 0.05 g/km (0.08 g/mi) with a catalyst. On the FTP, the total HC emissions were reduced from 0.06 g/km (0.09 g/mi) to 0.03 g/km (0.05 g/mi) with the AC Rochester and to 0.008 g/km (0.013 g/mi) with the JMI

catalyst. Considering methane and aldehyde emissions with the JMI catalyst (0.007 and 0.002 g/km, resp., Tables V and VI), the NMOG emissions are below the 0.025 g/km (0.040 g/mi) 50 K mile Ultra Low Emissions Standard required by California, but the NO<sub>x</sub> and PM are not.

On the Transit, the DOC similarly reduced the HC, CO and PM emissions, and the LNC reduced the NO<sub>x</sub> emissions, Table IIa. For example on the MVEG cycle, HC emissions were about 0.2 g/km without a catalyst and 0.08 g/km with the DOC and LNC. On the FTP, the Transit achieved 0.061 g/km for total HC and 0.066 g/km for NMOG, just above the 0.063 g/km (0.100 g/mi) NMOG 50 K mile Low Emissions Standard of California. On the FTP, the NO<sub>x</sub> emissions from the Transit were 1.14 g/km without catalyst and 0.19 g/km (0.3 g/mi) with both the DOC and urea LNC. This Transit does meet the 0.25 g/km (0.4 g/mi) NO<sub>x</sub> California 50 K mile Low Emission Standard.

On the European cycle, HC conversion efficiencies for the Sierra were 33% for the Degussa DOC and nearly the same at 43% ± 5% for the other DOC, Table III. Similarly the CO reductions were 50% for the Degussa DOC and 75% for the other DOC. The DOC provided no NO<sub>x</sub> conversion, but the PM conversions were between 9% and 15%.

On the FTP, the Sierra HC conversion efficiencies vary with the DOC and with the fuel sulfur, Table III. The JMI catalyst with 0.0 wt% fuel sulfur has the lowest emissions. The HC emissions appear limited by catalyst performance on the FTP, while they appear more independent of the catalyst on the European cycle.

Removing sulfur from the fuel hardly affects the Sierra emissions on the European test procedure, but it does on the FTP. Little difference was observed on the European cycle between the AC Rochester catalyst tested with 0.05 wt% fuel sulfur and the more active JMI catalyst tested with zero fuel sulfur suggesting that the emissions are not limited by the catalyst activity.

However, large differences were observed in the HC conversion on the FTP. It is unclear from these results, Table III, whether the

**Table II. Average Regulated Emissions (3 tests) and Standard Deviations  
from the Sierra With and Without Diesel Oxidation Catalysts (DOC)**

	MVEG				FTP			
After Treatment	HC g/km	CO g/km	NO <sub>x</sub> g/km	PM g/km	HC g/km	CO g/km	NO <sub>x</sub> g/km	PM g/km
none 0.0 wt% S	0.095 ±.011	0.466 ±.010	0.446 ±.063	0.059 ±.004	0.059 ±.007	0.428 ±.005	0.437 ±.007	0.055 ±.001
Degussa 0.05 wt% S	0.064 ±.004	0.247 ±.020	0.480 ±.015	0.066 ±.008	n.a.	n.a.	n.a.	n.a.
AC 0.05 wt% S	0.059 ±.005	0.117 ±.012	0.429 ±.018	0.054 ±.007	0.031 ±.006	0.045 ±.004	0.414 ±.012	0.050 ±.003
JMI 0.0 wt% S	0.049 ±.008	0.110 ±.013	0.487 ±.006	0.050 ±.002	0.008 ±.001	0.032 ±.013	0.435 ±.005	0.046 ±.002

**Table IIa. Average Regulated Emissions (3 tests) and Standard Deviations  
from the 1993 Transit With and Without a  
Urea Lean NO<sub>x</sub> and Oxidation Catalysts**

	MVEG				FTP			
	HC g/km	CO g/km	NO <sub>x</sub> g/km	PM g/km	HC g/km	CO g/km	NO <sub>x</sub> g/km	PM g/km
none	0.197 ±.007	0.960 ±.016	1.358 ±.036	0.217 ±.016	0.182 ±.010	0.736 ±.016	1.140 ±.018	0.132 ±.008
DOC	0.155 ±.007	0.747 ±.030	1.251 ±.061	0.163 ±.028	0.136 ±.003	0.540 ±.015	1.249 ±.249	0.108 ±.003
LNC + DOC	0.078 ±.009	0.785 ±.136	0.420 ±.035	0.105 ±.009	0.061 ±.004	0.482 ±.035	0.189 ±.008	0.087 ±.006

**Table III. Diesel Oxidation Catalyst (DOC) Conversions on the Sierra**

	MVEG				FTP			
Catalyst	HC %	CO %	NO <sub>x</sub> %	PM %	HC %	CO %	NO <sub>x</sub> %	PM %
Degussa 0.05 wt% S	33±12	47± 5	-8±18	-12±21	n.a.	n.a.	n.a.	n.a.
AC 0.05 wt% S	38±13	75± 3	4±18	9±18	47±16	90±1	5±4	8±7
JMI 0.0 Wt% S	49±14	76± 3	-9±17	15±9	86±3	93±3	1±3	17±4

catalyst change from AC to JMI or the fuel sulfur change had the greatest effect on FTP HC conversion. Other work with this identical Sierra and AC catalyst showed that reducing fuel sulfur from 0.05 wt% to 0.0 wt% gave a small increase in HC conversion on the FTP (2). This suggests that most of the HC conversion improvement, from 47% to 86% as seen in Table III, is due to catalyst activity.

On the Transit the urea LNC provides 69% and 84% NO<sub>x</sub> conversion for the European and Federal procedures, respectively, Table IIIa. As expected, the DOC alone provided no NO<sub>x</sub> conversion within experimental errors.

In addition on the 1993 Transit, the DOC gave PM conversion from 25% and 18% on the European and FTP cycles, respectively, and the DOC and LNC together gave 52% and 34%. These high PM conversions with the DOC and LNC are due to the abnormally large SOF in these 1993 Transit MVEG tests, Table Vb. The large volume of the LNC was particularly active in removing SOF. It is interesting to note that the LNC reduced the number of particles with diameters between 0.01 and 0.1 nm, Figure 3. Apparently the high SOF level deposited onto these particles as the exhaust was cooled in the dilution tube and sampling system.

**FUEL ECONOMY** - Compared to the 300 cells/in<sup>2</sup> substrates of the Degussa and JMI catalysts, slightly lower exhaust back pressures were experienced with either the blank exhaust pipe used to measure engine out and with the 400 cells/in<sup>2</sup> AC Rochester catalyst. This provided a barely detectable 4% ± 3% fuel economy increase on the Sierra on the European test procedure and none on the FTP, Table IV.

In addition, the large volume of the urea LNC reduces the exhaust back pressure on the 1993 Transit compared to the exhaust pipe used as baseline, thereby reducing the CO<sub>2</sub> emissions, especially on the European cycle, Table IV.

**HC SPECIATION** - While catalysts typically reduce total HC, LHC and SOF, one type of catalyst may be more effective at reducing short chain hydrocarbons while another may be more effective on longer chains. Of the exhaust hydrocarbons, volatile LHC have the shortest

chains; HC (as measured by the HFID) have the volatile LHC plus some longer semi-volatile chains, and SOF have the condensed longest chains. For the Sierra using 0.0 wt% S fuel on the MVEG, the DOC lowered LHC by 66%, total HC by 48% while it had no effect on SOF. The shortest chains were most active in this vehicle/catalyst. For the Transit on the MVEG, the DOC plus LNC lowered SOF by 90%, total HC by 60% and LHC by 58%. This is exactly the opposite order observed on the Sierra suggesting different mechanisms may be involved. Perhaps the LNC which is 10 times larger than the DOC was able to retain and oxidize more SOF, even some in aerosol form, because the very small particles had more time to diffuse to the catalyst walls.

SOF emissions from a vehicle are often highest at zero miles and decrease steadily to about 10,000 km, where they stabilize. The SOF emissions from the Sierra were low, 0.008 g/km, and stabilized; it had 25 K km. Within errors, the catalyst did not reduce SOF which remained at 0.008 ± 0.002 g/km. However, these low SOF emissions were near the detection limits and so the observed trends may be less accurate. On the other hand, the 1993 Transit had about 2 K km and larger SOF emissions, Table V. Here the catalysts reduced the SOF emissions.

With the 0.0 wt% S fuel on the FTP, methane emissions represented about 7.5% of the total HC without the catalyst and 31 % with the catalyst. In this case, the non-methane HC emissions are 0.006 g/km (0.01 g/mi).

**ALDEHYDES** - On the MVEG cycle, formaldehyde emissions from the Sierra were reduced from 0.0065 g/km to 0.004 or 0.0017 g/km by the AC and JMI catalysts respectively, Table VI where the mass of the oxygen is included the aldehyde emissions. On the FTP, Sierra formaldehyde emissions were reduced from 0.0042 g/km to 0.0011 and to 0.0008 g/km by the AC and JMI catalysts. These diesel formaldehyde emission levels with catalysts are comparable to those from the Current Gasoline AQIRP fleet, 0.001 g/km.

On the MVEG cycle, formaldehyde emissions from the 1993 Transit were reduced

**Table IIIa. Urea Lean NO<sub>x</sub> and Diesel Oxidation Catalyst Conversions  
on the 1993 Transit**

	MVEG				FTP			
	HC %	CO %	NO <sub>x</sub> %	PM %	HC %	CO %	NO <sub>x</sub> %	PM
DOC	21±6	22±5	8±7	25±18	25±6	27±4	-10±24	18±8
LNC + DOC	61±6	18±16	69±3	52±8	67±4	35±6	84±1	34±9

**Table IV. Carbon Dioxide Emissions and the Changes Therein**

Sierra					1993 Transit				
Catalyst	MVEG		FTP		Catalyst	MVEG		FTP	
	(g/km)	Change (%)	(g/km)	Change %		(g/km)	Change %	(g/km)	Change %
none	174±4		176±3		none	254±2		242±2	
Degussa	176±3		n.a.	n.a.	DOC	251±4	-1±3	244±4	1±2
AC	167±1	-4±3	173±1	-2±2	LNC+ DOC	241±2	-5±2	247±2	2±2
JMI	181±2	4±3	174±3	-1±3					

from 0.014 g/km to about 0.009 ± 0.002 g/km with the DOC alone or the DOC plus LNC. On the Federal cycle, formaldehyde emissions decreased from 0.012 g/km to 0.006 g/km with the DOC and to 0.005 with the both the DOC and LNC.

**OTHER TOXIC GASES** - On the FTP, benzene emissions from the Sierra are below 0.001 g/km with a catalyst, Table VII, well below the 0.007 g/km from the Current Gasoline AQIRP fleet. Benzene emissions from the 1993 Transit are below 0.002 g/km with a catalyst on the FTP, Table VIIa.

**PARTICULATE COMPOSITION** - The composition of the PM was analyzed for soot (elemental carbon or EC), SOF, including both condensed oil and fuel, sulfate and PAH. Other measurements have shown that each g of sulfate was associated with 2 g of water (3).

For the Sierra, the PM ranged from 0.05 to 0.059 g/km on the MVEG cycle and from 0.046 to 0.055 g/km on the FTP, Tables VIII and VIIIa. The lower particulate emissions were achieved with catalysts and zero sulfur

fuel. However, the sulfate in the particulate was not zero perhaps due to sulfur in the oil.

For the Sierra on both the European and Federal cycles, the mass of the EC was reduced by from 10% to 25% by the DOC while the SOF was unaffected. This result, which is contrary to conventional wisdom, suggests either EC measurement uncertainty or loss of some of the EC in the catalyst, where it may have been oxidized. As mentioned above, the SOF from the Sierra was quite low, near the level of detection, so simultaneous loss of SOF may be masked by errors. On the other hand perhaps, the SOF, which was deposited in the DOC, was volatilized and exited the DOC before it was oxidized. There is no clear difference in the particle size distribution for the Sierra with or without a catalyst, Figure 1.

For the 1993 Transit on both cycles, the SOF emissions were reduced by about 90% with both the LNC plus the DOC, while the EC

**Table V. Distribution of Organic Compounds for Sierra on MVEG Cycle  
with and without Diesel Oxidation Catalysts**

	HFID	CH <sub>4</sub>		LHC		SOF	
Catalyst	(g/km)	(g/km)	(%)	(g/km)	(%)	(g/km)	%
none 0.0 wt% S	0.095	0.012	12%	0.074	77%	0.007	8%
AC 0.05 wt% S	0.054	0.009	16%	0.038	70%	0.006	11%
JMI 0.0 wt% S	0.049	0.007	15%	0.025	52%	0.009	19%

**Table Va. Distribution of Organic Compounds for Sierra on FTP  
with and without Diesel Oxidation Catalysts**

	HFID	CH <sub>4</sub>		LHC		SOF	
Catalyst	(g/km)	(g/km)	(%)	(g/km)	(%)	(g/km)	%
none 0.0 wt% S	0.059	0.004	8%	0.053	90%	0.006	10%
AC 0.05 wt% S	0.031	0.005	17%	0.027	85%	0.006	18%
JMI 0.0 wt% S	0.009	0.003	31%	0.007	81%	0.006	66%

**Table Vb. Distribution of Organic Compounds for 1993 Transit on MVEG  
with and without Urea Lean NO<sub>x</sub> and Oxidation Catalysts**

	HFID	CH <sub>4</sub>		LHC		SOF	
Catalyst	(g/km)	(g/km)	%	(g/km)	%	(g/km)	%
none	0.197	0.015	8%	0.092	48%	0.128	65%
DOC	0.155	0.018	12%	0.102	65%	0.068	44%
LNC+DOC	0.078	0.004	5%	0.039	51%	0.013	17%

**Table Vc. Distribution of Organic Compounds for 1993 Transit on FTP  
with and without Urea Lean NO<sub>x</sub> and Oxidation Catalysts**

	HFID	CH <sub>4</sub>		LHC		SOF	
Catalyst	(g/km)	(g/km)	%	(g/km)	%	(g/km)	%
none	0.182	0.022	12%	0.078	43%	0.059	33%
DOC	0.136	0.012	9%	0.091	67%	0.035	32%
LNC+DOC	0.061	1.007	11%	0.035	58%	0.006	10%

**Table VI. Aldehyde Emissions from Sierra with and without Diesel Oxidation Catalysts**

Catalyst	MVEG			FTP		
	Total (g/km)	Formaldehyde (g/km)	Acetaldehyde (g/km)	Total (g/km)	Formaldehyde (g/km)	Acetaldehyde (g/km)
none 0.0 wt% S	0.0121	0.0065	0.0028	0.0101	0.0042	0.0025
AC 0.05 wt% S	0.0091	0.0040	0.0026	0.0036	0.0011	0.0009
JMI 0.0 wt% S	0.0040	0.0017	0.0012	0.0023	0.0008	0.0006

**Table VIa. Aldehyde Emissions from 1993 Transit with and without Urea Lean NO<sub>x</sub> and Oxidation Catalysts**

Catalyst	MVEG			FTP		
	Total (g/km)	Formaldehyde (g/km)	Acetaldehyde (g/km)	Total (g/km)	Formaldehyde (g/km)	Acetaldehyde (g/km)
none	0.0377	0.0144	0.0063	0.0326	0.0115	0.0058
DOC	0.0212	0.0073	0.0041	0.0183	0.0064	0.0033
LNC+DOC	0.0232	0.0106	0.0059	0.0134	0.0053	0.0041

**Table VII. Emissions of Other Toxic Gases from Sierra with and without Diesel Oxidation Catalysts**

Catalyst	MVEG		FTP	
	Benzene (g/km)	1,3 Butadiene (g/km)	Benzene (g/km)	1,3 Butadiene (g/km)
none 0.0 wt% S	0.0055	<0.0002	0.0017	<0.0002
AC 0.05 wt% S	0.0031	<0.0002	0.0008	<0.0002
JMI 0.0 wt% S	0.0027	<0.0002	0.0005	<0.0002

**Table VIIa. Emissions of Other Toxic Gases from 1993 Transit with and without Urea Lean NO<sub>x</sub> and Oxidation Catalysts**

Catalyst	MVEG		FTP	
	Benzene (g/km)	1,3 Butadiene (g/km)	Benzene (g/km)	1,3 Butadiene (g/km)
none	0.0044	<0.0002	0.0019	<0.0002
DOC	0.0056	<0.0002	0.0022	<0.0002
LNC+DOC	0.0015	<0.0002	0.0009	<0.0002

emissions were not. Here the emission levels are higher and therefore less sensitive to errors. The particle size distribution measurements show that the LNC plus DOC system substantially reduced the particles in the 0.01 to 0.1  $\mu\text{m}$  diameter range. Apparently this is where most of the SOF resides, possibly because it may condense on particles with the highest number density.

**PAH CONTENT** - With 0.0 wt% S fuel, the JMI catalyst lowered the Sierra PAH emissions by 65% for fluoranthene and pyrene over the MVEG cycle and by 35% over the FTP, Table IX. Similarly the BeP and BaP emissions were lowered by 85% on the MVEG and by about 40% over the FTP. On the 1993 Transit, the DOC lowered the PAH somewhat, but the combined LNC and DOC reduced the PAH by about 90%.

**PARTICLE SIZE DISTRIBUTION** - The particle size distributions were measured using an Electrical Aerosol Analyzer following a procedure described elsewhere (1,12). The number distribution showed a bimodal character with many particles in the 0.013 to 0.042  $\mu\text{m}$  size range and many in the 0.075 to 0.75  $\mu\text{m}$  range, but a minimum near 0.075  $\mu\text{m}$ , Figure 1 to 2. These modes are called nuclei and accumulation modes, respectively. On the FTP, 52% of the particle numbers from the Sierra without a catalyst were in the nuclei mode. With the AC catalyst, the number in the nuclei mode increased to 60%, and with the JMI catalyst the number in the nuclei mode decreased to 45%. The reasons for these inconsistent results are unclear.

Possible reasons may be that both the engine out and the JMI catalyst were tested without fuel sulfur, while the AC was tested with. Sulfate formed from the fuel sulfur may condense preferentially in the nuclei mode. Comparison of the size distributions with the JMI catalyst and without it, both of which were tested without fuel sulfur, show that the DOC decreased the fraction of particles in the nuclei mode. This automatically increased the fraction in the accumulation mode.

## **PARTICULATE TRAPS**

**REGULATED EMISSIONS** - The trap/regeneration systems reported here substantially reduced the

particulate emissions, Table X. The Transit with a DOC had 0.163 g/km and 0.108 g/km particulate emissions on the European and Federal procedures, respectively. With the Corning trap and either the Fe or K regeneration systems, these emissions were reduced to 0.04 g/km and 0.012 g/km on the European and Federal procedures, respectively. This is within a factor of 2 from gasoline vehicle particulate emissions which are about 0.005 g/km on the Federal procedure.

The Corning particulate traps provided from 75% to 80% particulate trapping efficiency on the European procedure and from 85% to 90% efficiency on the Federal procedure regardless of the regeneration system, Table XI. The SHW trap had somewhat lower trapping efficiency, 60%, on the European procedure but nearly equivalent efficiency, 85%, on the Federal procedure.

Each of the trap systems were regenerated during the testing procedure as evidenced by changes in back-pressure and by the release of extra CO. Indeed, for all of the regeneration systems, except for K, regeneration increased the CO emissions as evidenced by the negative CO conversion efficiencies. Apparently the K regeneration system provides some additional catalytic activity that helped eliminate the CO release.

**FUEL ECONOMY** - For unknown reasons, the fuel economy of the Corning trap with the K fuel additive was better than the other systems tested, Table XII. The fuel economies of the other systems were indistinguishable within errors from the base Transit.

**HC SPECIATION** - As expected, traps had little or no effect on the total HC or LHC, but they did reduce the SOF, Table XIII. On the MVEG cycle, the Corning traps plus DOC reduced the SOF from 0.128 g/km to about 0.03 g/km for the 1993 Transit. This was about a 75% reduction. The SHW trap plus DOC reduced the SOF by 60%. On the Federal cycle, the Corning traps plus DOC reduced the SOF from 0.059 g/km to 0.007 g/km. This was a 88% reduction in SOF which was nearly identical to the 90% reduction in PM provided by these traps.

**Table VIII. Particulate Composition from Sierra on MVEG  
with and without Diesel Oxidation Catalysts**

			SOF		Sulfate Fraction		
Catalyst	PM (g/km)	EC (g/km)	Oil (g/km)	Fuel (g/km)	SO <sub>4</sub> (g/km)	Water (g/km)	Sum/Pm (%)
none 0.0 wt% S	0.0586	0.0389	0.0025	0.0048	0.0023	0.0046	90.7
AC 0.05 wt% S	0.0536	0.0352	0.0017	0.0043	0.0029	0.0058	93.2
JMI 0.0 wt% S	0.0499	0.0294	0.0039	0.0055	0.0021	0.0042	90.3

**Table VIIIa. Particulate, Composition from Sierra on FTP  
with and without Diesel Oxidation Catalysts**

			SOF		Sulfate Fraction		
Catalyst	PM (g/km)	EC (g/km)	Oil (g/km)	Fuel (g/km)	SO <sub>4</sub> (g/km)	Water (g/km)	Sum/Pm (%)
none 0.0 wt% S	0.0547	0.0392	0.0015	0.0041	0.0015	0.0030	90.2
AC 0.05 wt% S	0.0504	0.0354	0.0026	0.0031	0.0028	0.0056	97.6
JMI 0.0 wt% S	0.0458	0.0302	0.0030	0.0030	0.0012	0.0024	86.9

**Table VIIIb. Particulate Composition from 1993 Transit on MVEG  
with and without Urea Lean NO<sub>x</sub> and Oxidation Catalysts**

			SOF		Sulfate Fraction		
Catalyst	PM (g/km)	EC (g/km)	Oil (g/km)	Fuel (g/km)	SO <sub>4</sub> (g/km)	Water (g/km)	Sum/Pm (%)
none	0.217	0.075	0.080	0.049	0.003	0.006	98%
DOC	0.163	0.075	0.048	0.020	0.003	0.006	93%
LNC+DOC	0.105	0.089	0.010	0.003	0.002	0.004	104%

**Table VIIIc. Particulate Composition from 1993 Transit on FTP  
with and without Urea Lean NO<sub>x</sub> and Oxidation Catalysts**

			SOF		Sulfate Fraction		
Catalyst	PM (g/km)	EC (g/km)	Oil (g/km)	Fuel (g/km)	SO <sub>4</sub> (g/km)	Water (g/km)	Sum/Pm (%)
none	0.131	0.063	0.037	0.023	0.002	0.005	99%
DO	0.108	0.061	0.019	0.016	0.002	0.004	94%
LNC+DOC	0.087	0.077	0.004	0.002	0.001	0.003	101%

**Table IX. PAH Emissions from Sierra with and without Diesel Oxidation Catalysts (in micrograms/km)**

Catalyst	MVEG				FTP			
	Fluoranthene (µg/km)	Pyrene (µg/km)	BaP (µg/km)	BeP (µg/km)	Fluoranthene (µg/km)	Pyrene (µg/km)	BaP (µg/km)	BeP (µg/km)
none 0.0 wt% S	3.01	3.65	0.22	0.47	3.46	3.75	0.28	0.45
AC 0.05 wt% S	1.18	1.18	0.17	0.51	1.93	2.22	0.22	0.65
JMI 0.0 wt% S	1.10	1.13	0.04	0.06	2.29	2.46	0.27	0.27

**Table IXa. PAH Emissions from 1993 Transit with and without Urea Lean NO<sub>x</sub> and Oxidation Catalysts (in micrograms/km)**

Catalyst	MVEG				FTP			
	Fluoranthene (µg/km)	Pyrene (µg/km)	BaP (µg/km)	BeP (µg/km)	Fluoranthene (µg/km)	Pyrene (µg/km)	BaP (µg/km)	BeP (µg/km)
none	6.86	4.93	0.07	0.24	4.83	4.17	0.23	0.48
DOC	5.54	4.26	0.01	0.24	3.18	2.26	0.03	0.22
LNC+DOC	0.62	0.48	0.05	0.07	0.24	0.19	0.02	0.04

**Table X. Average Regulated Emissions (3 tests) and Standard Deviations from the 1992 and 1993 Transits with and without Particulate Traps**

Vehicle/Trap	MVEG				FTP			
	HC g/km	CO g/km	NO <sub>x</sub> g/km	PM g/km	HC g/km	CO g/km	NO <sub>x</sub> g/km	PM g/km
'93/none	0.197 ±.007	0.960 ±.016	1.358 ±.036	0.217 ±.016	0.182 ±.010	0.736 ±.016	1.140 ±.018	0.131 ±.008
'93/DOC	0.155 ±.007	0.747 ±.030	1.251 ±.061	0.163 ±.028	0.136 ±.003	0.540 ±.015	1.249 ±.249	0.108 ±.003
'93/Corning Fe + DOC	0.157 ±.011	0.921 ±.016	1.255 ±.047	0.040 ±.009	0.124 ±.005	0.665 ±.008	1.019 ±.014	0.011 ±.001
'93/SHW Fe + DOC	0.157 ±.009	0.869 ±.028	1.068 ±.022	0.062 ±.012	0.139 ±.007	0.669 ±.010	0.958 ±.056	0.015 ±.0001
'93/Corning K + DOC	0.145 ±.018	0.747 ±.027	1.149 ±.033	0.036 ±.010	0.118 ±.003	0.479 ±.038	1.041 ±.011	0.012 ±.002
'92/none	0.135	0.824	1.049	0.139	0.117 ±.015	0.669 ±.026	0.810 ±.024	0.132 ±.0007
92/Corning elect.	0.123	0.976	0.749	0.027	0.125 ±.011	0.937 ±.114	0.749 ±.023	0.022 ±.005

**Table XI. Trap Conversion Efficiencies on the 1992 and 1993 Transit**

Vehicle/Trap	MVEG				FTP			
	HC %	CO %	NO <sub>x</sub> %	PM %	HC %	CO %	NO <sub>x</sub> %	PM %
'93/DOC	21±6	22±5	8±7	25±18	25±6	27±4	-10±24	18±8
'93/Corning Fe + DOC	-1±11	-23±7	0±9	76±10	9±5	-23±5	18±17	90±1
'93/SHW Fe + DOC	-1±10	-16±8	15±6	62±14	-2±7	-24±5	23±20	86±1
'93/Corning K + DOC	6±16	0±8	8±7	78±10	13±4	11±10	17±18	89±2
'92/Corning Elect	9	-19	29	81	-7±23	-40±23	8±6	84±4

**Table XII. Carbon Dioxide Emissions from the 1992 and 1993 Transits and Changes Therein**

Vehicle/Trap	MVEG		FTP	
	(g/km)	Change (%)	(g/km)	Change (%)
'93/none	254±2		242±2	
'93/DOC	251±4	1±3	244±4	-1±2
'93/Corning Fe + DOC	254±4	-1±3	249±3	-2±3
'93/SHW Fe + DOC	243±2	3±3	249±4	-2±3
'93/Corning K + DOC	239±3	5±3	236±3	4±3
'92/none	248		239±7	
'92/Corning Elect.	247	1	239±4	-0±4

**ALDEHYDES** - Traps have little or no effect on aldehyde emissions, Table XIV.

**OTHER TOXIC GASES** - Traps have little or no effect on benzene emissions, Table XV.

**PARTICULATE COMPOSITION** - The traps reduced both soot, or EC, and SOF, Table XVI. On the MVEG cycle, the EC was reduced from 0.075 g/km to 0.009 g/km, or by 88%, using the Corning traps. At the same 208 time, the PM and SOF were reduced by 77%

and 75%, respectively. On the Federal cycle, the EC was reduced from 0.063 g/km to 0.002 g/km, or by 97%, using the Corning traps. Similarly the PM and SOF were reduced by 90% and 88%, respectively. Clearly traps followed by a production DOC are more effective in lowering the emissions of EC than SOF.

**PAH CONTENT** - On both the MVEG and FTP cycles, the Corning traps with fuel additives reduced the PAH by 80% to 85%.

Table XVII. The Corning trap with electric regeneration reduced the PAH by 70% on the MVEG and by 80% to 85% on the FTP.

**Table Mill. Distribution of Organic Compounds for 1992 and 1993 Transits with and without Traps on MVEG Cycle**

	THC	CH <sub>4</sub>		LHC		SOF		Sum
Vehicle/Trap	(g/km)	(g/km)	(%THC)	(g/km)	(%THC)	(g/km)	(%THC)	(%THC)
'93/none	0.197	0.015	8%	0.092	48%	0.128	65%	113%
'93/DOC	0.155	0.018	12%	0.102	65%	0.068	44%	109%
'93/Corning Fe + DOC	0.157	0.015	10%	0.089	57%	0.034	22%	78%
'93/SHW Fe + DOC	0.157	0.015	10%	0.117	74%	0.050	32%	106%
'93/Corning K + DOC	0.145	0.016	11%	0.089	61%	0.024	17%	78%
'92/none	0.135	0.018	14%	0.076	56%	0.031	23%	79%
'9 Corning Elect	0.186	0.034	18%	0.127	68%	0.030	16%	84%

**Table XIIIa. Distribution of Organic Compounds for 1992 and 1993 Transits with and without Traps on FTP**

	THC	CH <sub>4</sub>		LHC		SOF		Sum
Vehicle/Trap	(g/km)	(g/km)	(%THC)	(g/km)	(%THC)	(g/km)	(%THC)	(%THC)
'93/none	0.182	0.022	12%	0.078	43%	0.059	33%	76%
'93/DOC	0.136	0.012	9%	0.091	67%	0.035	32%	99%
'93/Corning Fe + DOC	0.124	0.013	11%	0.083	67%	0.008	6%	73%
'93/SHW Fe + DOC	0.139	0.010	8%	0.092	67%	0.010	7%	73%
'93/Corning K + DOC	0.118	0.011	9%	0.079	67%	0.007	6%	73%
'92/none	0.117	0.014	12%	0.079	68%	0.022	19%	86%
'92/Corning Elect	0.125	0.013	10%	0.081	64%	0.005	4%	69%

**Table XIV. Aldehyde Emissions from the 1992 and 1993 Transits with and without Traps**

Vehicle/Trap	MVEG			FTP		
	Total (g/km)	Formaldehyde (g/km)	Acetaldehyde (g/km)	Total (g/km)	Formaldehyde (g/km)	Acetaldehyde (g/km)
'93/none	0.0377	0.0145	0.0063	0.0326	0.0115	0.0058
'93/DOC	0.0212	0.0073	0.0041	0.0183	0.0064	0.0033
'93/Corning Fe + DOC	0.0169	0.0085	0.0035	0.0132	0.0052	0.0035
'93/SHW Fe + DOC	0.0304	0.0086	0.0044	0.0121	0.0048	0.0029
'93/Corning K + DOC	0.0220	0.0080	0.0036	0.0197	0.0059	0.0035
'92/none	0.0145	0.0066	0.0035	0.0121	0.0054	0.0031
'92/Corning Elect	0.0202	0.0075	0.0038	0.0193	0.0053	0.0026

**Table XV. Emissions of Other Toxic Gases from 1992 and 1993 Transits with and without Traps**

Vehicle/Trap	MVEG		FTP	
	Benzene (g/km)	1,3 Butadiene (g/km)	Benzene (g/km)	1,3 Butadiene (g/km)
'93/none	0.0044	<0.0002	0.0019	<0.0002
'93/DOC	0.0058	<0.0002	0.0021	<0.0002
'93/Corning Fe + DOC	0.0029	<0.0002	0.0027	<0.0002
'93/SHW Fe + DOC	0.0041	<0.0002	0.0037	<0.0003
'93/Corning K + DOC	0.0034	<0.0002	0.0024	<0.0002
'92/none	0.0046	<0.0002	0.0008	<0.0002
'92/Corning Elect	0.0044	<0.0002	0.0020	<0.0002

**Table XVI. Particulate Composition from the 1992 and 1993 Transits  
on MVEG with and without Traps**

Catalyst	PM (g/km)	EC (g/km)	SOF		Sulfate Fraction		
			Oil (g/km)	Fuel (g/km)	SO <sub>4</sub> (g/km)	Water (g/km)	Sum/Pm (%)
'93/none	0.217	0.074	0.080	0.049	0.003	0.006	97.6
'93/DOC	0.163	0.075	0.048	0.020	0.003	0.006	92.9
'93/Corning Fe + DOC	0.040	0.008	0.017	0.017	0.002	0.003	118.6%
'93/SHW Fe + DOC	0.062	0.010	0.033	0.016	0.002	0.003	105.0%
'93/Corning K + DOC	0.036	0.009	0.016	0.007	0.002	0.004	104.4%
'92/none	0.139	0.094	0.014	0.017	0.002	0.005	95.1%
'92/Corning Elect	0.054	0.017	0.006	0.028	0.003	0.006	111.4%

**Table XVIa. Particulate Composition from the 1992 and 1993 Transits  
on FTP with and without Traps**

Catalyst	PM (g/km)	EC (g/km)	SOF		Sulfate Fraction		
			Oil (g/km)	Fuel (g/km)	SO <sub>4</sub> (g/km)	Water (g/km)	Sum/Pm (%)
'93/none	0.131	0.063	0.037	0.023	0.002	0.005	98.9%
'93/DOC	0.108	0.061	0.019	0.016	0.002	0.004	94.3%
'93/Corning Fe + DOC	0.011	0.002	0.003	0.005	0.002	0.003	140.4%
'93/SHW Fe + DOC	0.015	0.003	0.005	0.006	0.001	0.003	113.0%
'93/Corning K + DOC	0.012	0.003	0.003	0.004	0.002	0.004	133.4%
'92/none	0.132	0.094	0.009	0.013	0.002	0.004	92.4%
'92/Corning Electric	0.024	0.010	0.001	0.004	0.001	0.003	80.0%

**Table XVII. PAH Emissions from the 1992 and 1993 Transits  
with and without Traps (in micrograms/km)**

Vehicle/Traps	MVEG				FTP			
	Fluoranthene ( $\mu\text{g}/\text{km}$ )	Pyrene ( $\mu\text{g}/\text{km}$ )	BaP ( $\mu\text{g}/\text{km}$ )	BeP ( $\mu\text{g}/\text{km}$ )	Fluoranthene ( $\mu\text{g}/\text{km}$ )	Pyrene ( $\mu\text{g}/\text{km}$ )	BaP ( $\mu\text{g}/\text{km}$ )	BeP ( $\mu\text{g}/\text{km}$ )
'93/none	6.86	4.93	0.07	0.24	4.83	4.17	0.23	0.48
'93/DOC	5.54	4.26	0.04	0.24	3.14	2.26	0.03	0.22
'93/Corning Fe + DOC	1.19	1.07	0.03	0.20	0.88	0.76	0.02	0.17
'93/SHW Fe + DOC	1.19	0.93	0.10	0.35	0.69	0.52	0.10	0.34
'93/Corning K + DOC	0.91	0.81	0.00	0.13	0.88	0.76	0.05	0.08
'92/none	5.92	4.44	0.00	0.58	3.73	3.13	0.0	0.39
'92/Corning Elect	1.82	1.26	0.02	0.05	0.64	0.50	0.0	0.0

**PARTICULATE SIZE DISTRIBUTION** - For the FTP, the Transit engine-out, particle size distribution had 58.6% of the particles in the nuclei mode. When Corning traps were added with a DOC the number of particles in the nuclei mode increased to 88.1%, 95.7% and 99.3 with the Fe, K and electrical regeneration systems, respectively, Figures 3 and 4. With the SHW trap the fraction of particles in the nuclei mode was 58.9%, the same as without a trap. With the urea LNC, the fraction of particles in the nuclei mode was only 23.3%. This substantial loss in the nuclei mode fraction was the largest change of the number distribution observed.

## SUMMARY

The detailed regulated and non-regulated emissions from three vehicles, a Sierra and two Transits, with several diesel oxidation catalysts (DOC), one urea lean  $\text{NO}_x$  catalyst (LNC) and several particulate traps have been measured both on the European MVEG and the U. S. FTP cycles. This report evaluates these aftertreatment methods as methods to reduce the emissions from current diesel vehicles below those of comparable gasoline vehicles. Current diesel vehicles equipped only with DOC have lower emissions than those of gasoline except for  $\text{NO}_x$ , PM and formaldehyde (1).

A Sierra at 1360 kg inertia weight was selected as a typical passenger car and was used to test improved DOC. Two Transits at 1810 inertia were selected as typical light-trucks and were used to test traps and LNC because of time needed to install them and the space they required.

On the Sierra, the maximum HC CO, PM and formaldehyde conversions obtained with a DOC on the FTP was 86%, 93%, 17% and 81% respectively, with Swedish Class 1 fuel without sulfur, and 62%, 89%, 19% and 74% with the same fuel doped to 0.05 wt% sulfur, Table XVIII. On a Transit, the maximum  $\text{NO}_x$  conversion measured on the FTP was 84% with the urea LNC, and the maximum particle trapping efficiencies on the FTP was 89% with the Corning trap.

On the FTP, the lowest HC formaldehyde and CO emissions were observed on the Sierra; they were 0.008 g/km (0.013 g/mi), 0.0008 g/km (0.0013 g/mi) and 0.032 g/km (0.51 g/mi), respectively. The lowest  $\text{NO}_x$  emissions was observed on the 1993 Transit

Table XVIII. Best FTP Performance, Conversion and Trapping Efficiencies, of the Aftertreatment Systems Tested				
Emission	DOC (.0 wt% S)	DOC (.05 wt% S)	Urea LNC + DOC (.05wt% S)	Trap K + DOC (.05wt% S)
HC	86%	62%	67%	13%
CO	93%	89%	35%	10%
NO <sub>x</sub>	0%	0%	84%	0%
PM	17%	19%	34%	89%
EC	24%	10%	0%	95%
SOF	0%	0%	90%	88%
Formaldehyde	81%	74%	54%	49%

with the urea LNC; it was 0.189 g/km (0.30 g/mi). If the same NO<sub>x</sub> conversion, 84%, could be obtained on the Sierra, the NO<sub>x</sub> emissions would be 0.070 g/km (0.11 g/mi) because its NO<sub>x</sub> feedgas level is lower. The lowest PM emissions on the FTP was observed on the 1993 Transit; it was 0.011 g/km (0.018 g/mi). Similarly if the same trapping efficiencies, 90%, could be obtained on the Sierra, the PM emissions would be 0.005 g/km (0.007 g/mi).

Combining these best results, the FTP emissions from the Sierra using Swedish Class 1 fuel would be 0.008 g/km (0.013 g/mi), 0.032 g/km (0.051 g/mi), 0.070 g/km (0.11 g/mi) and 0.005 g/km (0.007 g/mi) for HC CO, NO<sub>x</sub> and PM, respectively. The corresponding methane, formaldehyde and total aldehyde emissions are 0.003 g/km (0.005 g/mi), 0.0008 g/km (0.0013 g/mi) and 0.002 g/km (0.004 g/mi), respectively. The California NMOG emissions were 0.007 g/km (0.012 g/mi), where NMOG is equal to total HC minus methane plus total aldehydes. These emissions are well below the California

ULEV standards and suggest that a ULEV diesel passenger car is possible. However, it must be emphasized that it may not be possible to achieve these lowest HC, CO, NO and PM emissions simultaneously. Trying to do this requires a complicated, expensive, three-component aftertreatment system with a urea LNC, a DOC and a particulate trap. This combined system would require several compromises dictated by cost and packaging that would decrease the overall performance. In addition, the urea LNC and the traps with Fe and K regeneration may not be practical options on customer vehicles because they require additional fluids, i.e., urea, ferrocene, etc. solutions, on-board. How to maintain an adequate urea supply on customer vehicles over several years is uncertain. Finally the durability of such a complex system remains an open issue.

Still with the above qualifications, technology exists that if perfected may make diesel passenger car emissions comparable to gasoline emissions while at the same time preserving most of the fuel economy gains expected from diesels.

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